NRL Memorandum Report 4927

The Fundamentals of the 3914Å and 3371Å Emissions for N_2 and Air Plasma Diagnostics

A. W. ALI

Plasma Physics Division

October 25, 1982

This report was sponsored by Defense Advanced Research Projects Agency (DoD), DARPA Order No. 3718, monitored by NSWC under Contract No. N60921-81-WR-W0190.

NAVAL RESEARCH LABORATORY
Washington, D.C.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Memorandum Report 4927	2. GOVT ACCESSION NO. A120587	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE FUNDAMENTALS OF THE 3914Å AND 3371Å EMISSIONS FOR N_2 AND AIR PLASMA DIAGNOSTICS		5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL problem. 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) A.W. Ali		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61101E; 47-0900-0-2
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Advanced Research Projects Agency Arlington, VA 22209		12. REPORT DATE October 25, 1982 13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Naval Surface Weapons Center Silver Spring, MD 20910		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

This report was sponsored by Defense Advanced Research Projects Agency (DoD), DARPA Order No. 3718, monitored by NSWC under Contract No. N60921-81-WR-W0190.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Plasma diagnostics
3914Å
3371Å
Excitation cross section
Quenching coefficient

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A review is made of the basic physics of emission at 3914Å and 3371Å. The excitation cross section, the quenching coefficient and other mechanisms that affect these emissions are discussed in detail.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

CONTENTS

THE FUNDAMENTALS OF THE 3914Å AND 3371Å EMISSIONS FOR N_2 AND AIR PLASMA DIAGNOSTICS

1. INTRODUCTION

The interaction of an electron beam with gaseous elements generates a plasma and characteristic emission spectra which are unique to each element. The emission is over a wide range of the electromagnetic radiation, from extreme ultraviolet to long wave infrared, consisting of band, line, and continuum emissions. Such a spectrum provides important information for measuring various plasma parameters without perturbing the state of the plasma.

Emission from an air plasma, is a complex phenomena arising from a host of excitation mechanisms. These mechanisms are numerous and are reviewed briefly. However, the main emphasis will be on two molecular bands at 3371Å and 3914Å . Their excitation mechanisms and other processes that affect their intensities are discussed in detail. The basic understanding of these mechanisms provides the tools for the plasma modelling and its diagnostics.

2. EMISSION PROCESSES IN AIR

Emission from air falls into bands, lines and continuum emissions. The processes that lead to the band emissions are

1. Simultaneous Excitation and Ionization

$$e + M_2 \rightarrow (M_2^+)^* + 2e \tag{1}$$

Examples are: the First Negative and Meinel Bands of N_2^+

2. Direct Excitation

$$e + M_2 \rightarrow (M_2)^* + e \tag{2}$$

Manuscript submitted August 24, 1982.

Examples of this excitation are the First and Second Positive Band Systems of N_2.

3. Ground State Vibrational Excitation

$$e + MK \rightarrow MK^{\neq} + e \tag{3}$$

$$e + (MK^{+}) \rightarrow (M_2^{+})^{\neq} + e \tag{4}$$

Examples are infrared bands of NO and NO^+.

4. Atom - Atom Interchange or Chemiluminescence

$$K^{*} + M_2 \rightarrow MK^{*} + M \tag{5}$$

Examples are infrared emissions from NO.

In the preceding equations K^* and $M_2{}^*$ indicate excited atoms and molecules, respectively. $M_2^{\neq}$ is a vibrationally excited molecule. It should be noted, however, that the electronically excited molecules in reactions 1 and 2 can be vibrationally excited as well.

The line emissions arise when an excited atom or atomic ion is generated and that the excitation energy or part of it is emitted as radiation. These excited states are produced by

1. Dissociative Excitation and Dissociative Ionization With Excitation

$$e + M_2 \rightarrow (M)^* + M + e \tag{6}$$

$$e + M_2 \rightarrow (M)^* + M^+ + 2e \tag{7}$$

$$e + M_2 \rightarrow M + (M^+)^* + 2e \tag{8}$$

Examples for the first process is the emissions at 8447Å from the dissociation of O_2. Emissions at 8210Å from N and 5003Å from N^+ due to dissociative and ionization excitation of N_2 illustrate emission processes in reactions 7 and 8, respectively.

2. Direct Excitation

$$e + M \rightarrow M^* + e \tag{9}$$

$$e + M^+ \rightarrow (M^+)^* + e \tag{10}$$

3. Dissociative Recombination

$$e + M_2^+ \rightarrow M^* + M \tag{11}$$

4. Radiative and Collisional Recombination

$$e + M^{+} \rightarrow M^{*} + h\nu \tag{12}$$

$$e + e + M^{+} \rightarrow M^{*} + e + h\nu \tag{13}$$

$$e + M + M^{+} \rightarrow M^{*} + M + h\nu \tag{14}$$

The continuum emission, on the other hand, results from free - free transitions of the thermal electrons in the field of the atomic and molecular ions as well as in the field of the atoms and molecules e. g.

$$e + M^{+} \rightarrow e + M^{+} + h\nu \tag{15}$$

$$e + M_2^{+} \rightarrow e + M_2^{+} + h\nu \tag{16}$$

$$e + M \rightarrow e + M + h\nu \tag{17}$$

$$e + M_2 \rightarrow e + M_2 + h\nu \tag{18}$$

3. SELECTED BANDS FOR PLASMA DIAGNOSTICS

The nitrogen molecule, N_2 and its ion, N_2^{+} have numerous bands which emit radiation in the ultraviolet, visible and infrared. Many of these bands can be used for diagnostics of N_2 and air plasmas. However, two specific bands shown in Figure 1, the first negative and the second positive, have often been utilized for plasma diagnostics [2-8] and as a measure of electron and x-ray energy deposition in N_2 and Air. Therefore, a review of the basic

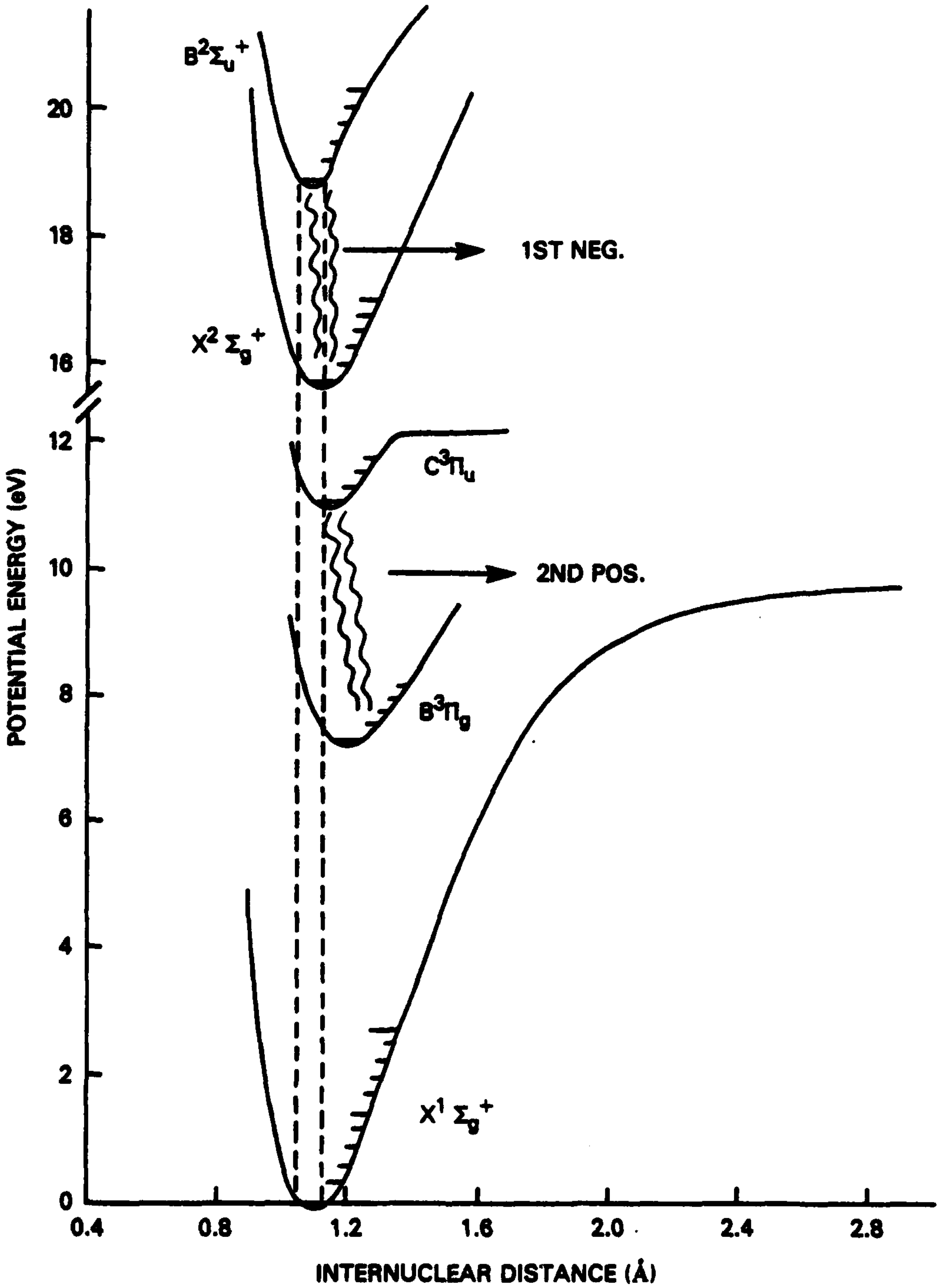

Fig. 1 — The partial potential energy diagram of N_2 and N_2^+. Partial emissions in the second position and first negative bands are indicated.

physical processes affecting their excitations and decays is in order.

3.1 THE (0,0) BAND OF THE FIRST NEGATIVE BANDS SYSTEM OF N_2^+

The first negative bands system of N_2^+ corresponds to the $B\,^2\Sigma\,(v') \rightarrow X\,^2\Sigma\,(v'')$ transitions. The transition rates from various B-state vibrational levels have been calculated [10,11] and measured [12,13]. The transitions from $\bar{v}=0$ have strong emissions at 3914Å, 4278Å and 4708Å which correspond to the (0,0), (0,1) and (0,2) bands, respectively. The lifetime of the B ($v'=0$) state has been measured by many investigators and a weighted average[14] is 62.5×10^{-9} sec. using the Franck-Condon factor[11] for the (0,0) transition and the weighted average for the lifetime of the $v'=0$ state, one obtains a rate of 1.04×10^{7} sec.$^{-1}$ for the (0,0) transition at 3914Å.

3.1.1 THE QUENCHING OF THE N_2^+ (B, $v'=0$)

The N_2^+ (B, $v'=0$) state is quenched in collisions with N_2 and O_2 according to the following two body processes:

$$N_2^+\,(B,0) + N_2 \rightarrow N_2^+\,(X) + N_2 \qquad (19)$$

$$N_2^+\,(B,0) + O_2 \rightarrow N_2^+\,(X) + O_2 \qquad (20)$$

There is evidence [15] that the (B,0) state is also quenched by the following three body process

$$N_2^+\,(B,0) + M + O_2 \rightarrow N_2^+\,(X) + N_2 + O_2 \qquad (21)$$

where M indicates N_2 and/or O_2, i.e. the third body in this reaction must be O_2.

The rate coefficient for Reactions (19) and (20) have been measured by

Mitchell[15], Brucklehurst and Downing[16], Hirsh et al[17], and Mackay and March[18]. The last measurement[18] which measures the quenching by N_2 only gives two different values which differ by 40% and thus are not included in Table 1 where the other measurements are summarized.

Table 1:

The Quenching Coefficient for the $B\,^2\Sigma\,(v'=0)$ State (in $Torr^{-1}$)

	Ref. 15	Ref. 16	Ref. 17
N_2	0.96 ± 0.09	0.85 ± 0.3	0.95 ± 0.05
O_2	$1.56 \pm 0.15^{(*)}$	0.84 ± 0.3	1.5 ± 0.6

A weighted average for the quenching rate coefficients of the $(v'=0)$ state by N_2 and O_2 are 4.6×10^{-10} cm^3/sec and 6.5×10^{-10} cm^3/sec, respectively.

As for the three body quenching process given by Equation (21), Mitchell[15] gives a value of 3.1×10^{-29} cm^3/sec for both O_2 and N_2.

3.1.2 THE EXCITATION PROCESSES OF $N_2^+(B, v'=0)$

The $N_2^+(B)$ state is excited by the direct ionization and excitation process (See Eq. 1) whenever the incident electron has an energy above the threshold energy for the process (>18.8eV) . Since the (0,0) transition at 3914Å is a well known auroral emission[19], it has attracted considerable interest and its cross section has been measured by many investigators. The emission cross section at 3914Å, for the direct excitation and ionization of N_2, is shown in Figure 2, based mainly on the data of reference 27.

(*) Data for O_2 was obtained from air and N_2 data

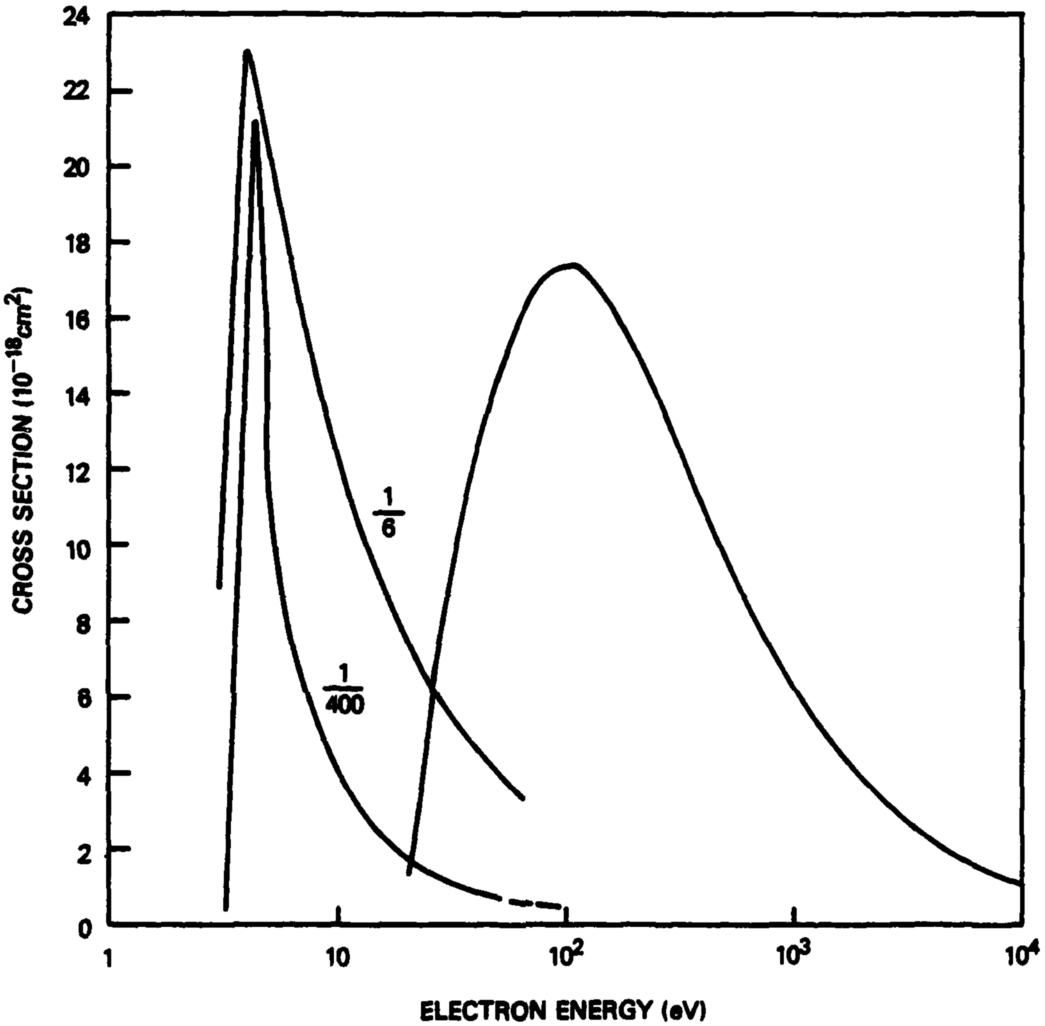

Fig. 2 — The 3914Å emission cross section due to electron impact with N_2 (curve 1) and N_2^+ (curves 1/6 and 1/400). The last two curves, from reference 28 and 29, are reduced for comparison by factors of 6 and 400, respectively.

However, the $B\,^2\Sigma(v')$ state can be excited by electron impact from the nd state of the nitrogen ion, $N_2^+(x,v'')$, where the excitation threshold is .16 eV. The cross section for this process has been measured by Lee and ton[28] and by Crandall, et al[29]. These two measurements are also shown in re 2, one of these[23] may be too large as indicated by McLean, et al[30].

THE (0,0) BAND OF THE SECOND POSITIVE BANDS SYSTEM OF N_2

The second positive system of N_2 corresponds to the $C\,^3\pi(v') \rightarrow B\,^3\pi(v'')$ sitions. The life times of the various $C\,^3\pi$ vibrational levels have been ured[12,13] and calculated[10,11]. A weighted average[14] of many measurements s a life time of 36.6 nsec for the $v'=0$ state. The transition's from the $(v'=0)$ state have strong emissions at 3371Å, 3577Å and 3805Å which espond to the (0,0), (0,1) and (0,2) bands, respectively. Using the ck-Condon Factors[31] for the (0,0) transitions and the life time of the 0) state one obtains a transition rate of 1.22×10^{7} sec^{-1} for the (0,0) sitions at 3371Å.

1 THE QUENCHING OF $N_2(C,v'=0)$

The $C\,^3\pi\,(v'=0)$ state is quenched in collisions with N_2 and O_2 according to following two processes.

$$N_2[C\,^3\pi(v'=0)] + N_2 \rightarrow N_2 + N_2 \tag{22}$$

$$N_2[C\,^3\pi(v'=0)] + O_2 \rightarrow N_2 + O_2 \tag{23}$$

rate coefficient for these reactions have been measured in nitrogen and by Mitchell[15], Millett, et al[32], Albugues, et al[33] and Brocklehurst and ing[16]. These measured data are summarized in Table II.

Table II:

Quenching Coefficient for $C^3\pi(v'=0)$ in Units of $10^{-11}cm^3/sec$.

	Ref. 15	Ref. 16	Ref. 32	Ref. 33
N_2	(1.12 ± .143)	(1.17 ± 0.137)	(1.15 ± .062)	(1.15 ± 0.062)
O_2	31.2 ± 0.96	-	(29 ± 1.8)	27.9

A recommended value for quenching of $C^3\pi$ $(v'=0)$ is 1.12×10^{-11} cm^3/sec. As for quenching by O_2 we recommend a value of 2.9×10^{-10} cm^3/sec after lowering the values of Ref. 15 by 1.2 and raising the values of Ref. 32 and 33 by 1.2 because of the different life-times utilized in these references compared to an average life time of 36.5 nsec.

3.2.2 THE EXCITATION PROCESSES OF N_2 $(C, v'=0)$

The upper level of the second positive band system, $C^3\pi$, is excited by electron impact from the ground state of N_2. The cross section for the excitation of the C-state has been measured and calculated by numerous investigators, see Ref. 34 for details. Since the excitation is a transition from a singlet, $^1\Sigma$, to a triplet, $^3\pi$, state, it is sharply peaked near the excitation threshold and varies as $\sim E^{-3}$ where E is the energy of the incident electron. In Figure 3 we show the emission cross section for the (0,0) transition at 3371Å as measured by Imami and Borst[35].

The excitation threshold for the $C^3\pi$ $(v'=0)$ is $\sim$ 11eV and in a plasma it is generally excited by the secondary and the plasma electrons which also excite other triplet status of N_2, e.g. $A^3\Sigma$ and $B^3\pi$ states. Therefore, the effects of excitations from the A + B + C state should be investigated and may become appreciable, depending on the state of the plasma. Furthermore, collisions with excited states i.e. $N_2(C)$ with $N_2(C)$, $N_2(B)$ and $N_2(A)$ may

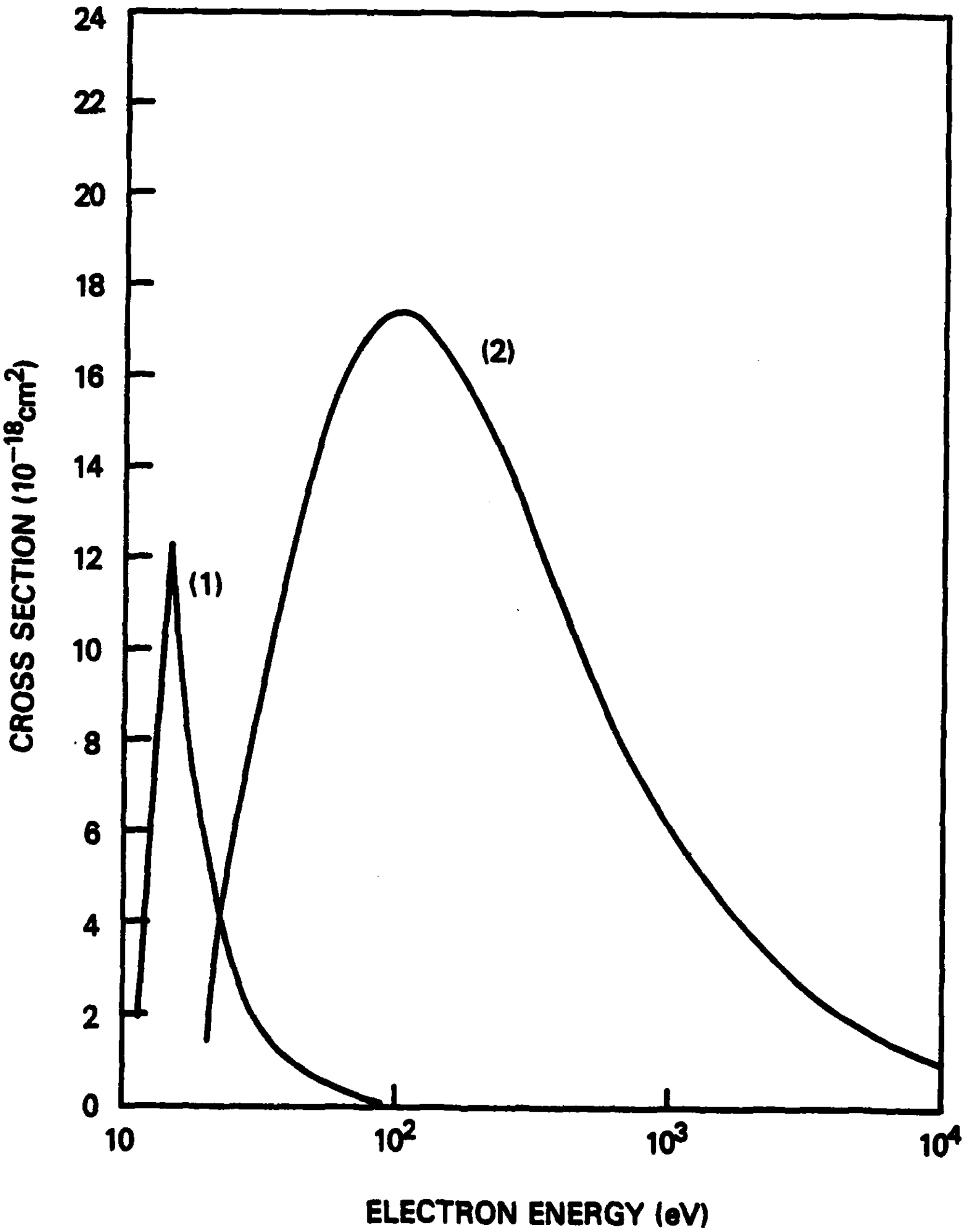

Fig. 3 — The emission cross sections of 3371Å (curve 1) and 3914Å (curve 2)

deplete the C-state as do the superelastic collisions with low energy electrons. In a cold plasma and at pressures where N_4^+ predominates, the dissociative recombination of N_4^+ may lead to the population of the C-state. R. Hill[36] has reported that 3% of this dissociative recombination results in the population of the C ($v'=0$) .

In terms of what other processes may affect the emission at 3371Å, it should be noted that this band is a well known laser. It was first discovered by Heard (1963) and has been investigated throughly in pure nitrogen, where excitation occurs by electron beams[38] and in electric discharges with a fast current rise time[39,40]. Lasing action has also been observed in air[41,42] and under atmospheric conditions. Since this laser is a superradiant, stimulated emission also affects the population density of the $v'=0$ state and hence its emission.

REFERENCES

1. R. W. B. Pearse and A. G. Gaydon "Identification of Molecular Spectra" Wiley (1963) New York.

2. F. Cramarossa, G. Ferraro and E. Molinari, J. Quant. Spect. Rad. Transfer 14, 419 (1974).

3. F. Cramarossa, S. Benedicti and G. Ferraro, J. Quant. Spect. Rad. Transfer 23, 291 (1980).

4. V. N. Ochkin, S. Y. Savinov and N. N. Sobolev, Soviet Phys. JETP 48, 232 (1978).

5. O. V. Ravodina, T. N. Popova, and N. A. Prilezhaeva, Soviet Optics & Spectrosc. 40, 452 (1976).

6. A. E. Kassem and R. S. Hichman, Physics of Fluids 17, 1976 (1974).

7. T. Sakuta, Y. Kito, and I. Miyachi, IEEE Trans. Plasma Science PS8, 29 (1980).

8. A. D. Kosoruchkina and E. S. Trekhtov, Soviet Optics and Spectrosc. 49, 25 (1981).

9. D. E. Shemansky, T. M. Donahue and E. C. Zipf, Planet. Spac. Sc., 20, 905 (1972) and references therein.

10. R. W. Nicholls, J. Atm. Terrest. Phys. 25, 218 (1963).

11. D. C. Jain and R. C. Sahni, Int. J. Quantum Chemistry 1, 721 (1967).

12. R. G. Bennett and F. W. Dalby, J. Chem. Phys. 31, 434 (1959).

13. M. Jeunehomme, J. Chem. Phys. 44 2672 (1966)

14. For further information see e. g. A. Lofthus and P. H. Krupenie, J. Chem. Ref. Data 6, 113 (1977).

15. K. B. Mitchell, J. Chem. Phys. 53,1795 (1970)

16. B. Brocklehurst and F. A. Downing, J. Chem. Phys. 46, 2976 (1967).

17. M. N. Hirsch, E. Poss and P. N. Eisener, Phys. Rev. A 1, 1615 (1970).

18. G. I. Mackay and R. E. March, Can. J. Chem. 49, 1268 (1971).

19. A. Omholt, "The Optical Aurora", Springer-Verlag, New York (1971).

20. D. T. Stewart, Proc. Phys. Soc. 69, 437 (1956).

21. S. Hayakawa and H. Nishimura, J. Geomag. Geoelect. (Japan) 16, 72 (1964).

22. J. W. McConkey and I. D. Latimer, Proc. Phys. Soc. 86, 463 (1965).

23. B. N. Srivastava and I. M. Mirza, Phys. Rev. 168, 86 (1968).

24. J. W. McConkey, J. M. Latimer and D. J. Burns, Planet Space Sci. 15, 1332 (1967).

25. R. F. Holland, Los Alamos Scientific Lab Report LA - 3783 (1967).

26. J. F. M. Aarts, F. J. DeHeer and D. A. Vroom, Physica 40, 197 (1968).

27. W. L. Borst and E. C. Zipf, Phys. Rev. A, 1, 834 (1970).

28. A. R. Lee and N. P. Carlton, Physics. Lett. 27A, 195 (1968).

29. D. H. Crandall, W. E. Kauppila, R. A. Phaneuf, P. O. Taylor and G. H. Dunn, Phys. Rev. A9, 2545 (1974).

30. E. A. McLean, A. W. Ali, J. A. Stamper and S. O. Dean, Physics Letters 38A, 209 (1972).

31. W. Benesch, J. T. Vanderslice, S. G. Tilford and P. G. Wilkinson, Astophys. J., 144, 408 (1966).

32. P. Millet, Y. Salamero, H. Brunet, J. Galy and D. Blanc, J. Chem. Phys. 58, 5839 (1973).

33. F. Albugues, A. Birot, D. Blanc, H. Brunet, J. Galy, P. Millet and J. L. Teyssier, J. Chem. Phys. 61, 2695 (1974).

34. A. W. Ali, "Excitation and Ionization Cross Sections for Electron Beam and Microwave Energy Deposition in Air", NRL Memo Report 4598 (1981).

35. M. Imami and W. Borst, J. Chem. Phys. 61, 1115 (1974).

36. R. Hill, Stanford Research Institute, Private Communication (1981).

37. H. G. Heard, Nature, 200, 667 (1963).

38. D. A. McArthur and J. W. Poukey, IEEE, J. Quant. Electron QE11, 892 (1975).

39. J. D. Shipman, J. Appl. Phys. Lett 10, 3 (1967).

40. D. A. Leonard, Appl. Phys. Lett. 7, 4 (1965).

41. A. Svedberg, L. Hogberg, and R. Nilsson, Appl. Phys. Lett. 12, 102 (1968).

42. W. Herdon, Phys. Letts.54, 96 (1975).

DISTRIBUTION LIST

Commander
Naval Sea Systems Command
Dept. of the Navy
Washington, D.C. 20363
ATTN: NAVSEA 03H (Dr. C. F. Sharn)

Air Force Weapons Laboratory
Kirtland Air Force Base
Albuquerque, New Mexico 87117
ATTN: Maj. H. Dogliani
Dr. K. Dreyer
Dr. D. Straw

U.S. Army Ballistics Research Laboratory
Aberdeen Proving Ground, Maryland 21005
ATTN: Dr. D. Eccleshall (DRXBR-BM)

Ballistic Missile Defense Advanced Technology Center
P.O. Box 1500
Huntsville, Alabama 35807
ATTN: Dr. L. Harvard (BMDSATC-1)

B-K Dynamics Inc.
15825 Shady Grove Road
Rockville, Maryland 20850
ATTN: Mr. I. Kuhn

Lawrence Livermore Laboratory
University of California
Livermore, California 94550
ATTN: Dr. R. J. Briggs
Dr. T. Fessenden
Dr. E. P. Lee
Dr. S. Yu

Mission Research Corporation
735 State Street
Santa Barbara, California 93102
ATTN: Dr. C. Longmire
Dr. N. Carron
Dr. M. Schiebe

National Bureau of Standards
Gaithersburg, Maryland 20760
ATTN: Dr. Mark Wilson

Science Applications, Inc.
Security Office
5 Palo Alto Square, Suite 200
Palo Alto, California 94304
ATTN: Dr. R. R. Johnston
Dr. Leon Feinstein
Dr. D. Keeley

Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910
ATTN: Mr. R. J. Biegalski
Dr. C. M. Huddleston
Dr. M. H. Cha
Dr. H. S. Uhm
Dr. R. B. Fiorito
Dr. R. Cawley

C. S. Draper Laboratories
Cambridge, Massachusetts 02139
ATTN: Dr. E. Olsson
Dr. L. Matson

Physical Dynamics, Inc.
P. O. Box 1883
La Jolla, California 92038
ATTN: Dr. K. Brueckner

Office of Naval Research
Department of the Navy
Arlington, Virginia 22217
ATTN: Dr. W. J. Condell (Code 421)
Dr. T. Berlincourt (Code 464)

Avco Everett Research Laboratory
2385 Revere Beach Pkwy.
Everett, Massachusetts 02149
ATTN: Dr. R. Patrick
Dr. Dennis Reilly

Defense Technical Information Center
Cameron Station
5010 Duke Street
Alexandria, VA 22314 (2 copies)

Naval Research Laboratory
Washington, D.C. 20375
ATTN: M. Lampe - Code 4792
J. R. Greig - Code 4763
T. Coffey - Code 4000
S. Ossakow - Code 4700 (26 copies)
Library - Code 2628 (20 copies)
A. Ali - Code 4700.1 (30 copies)
B. Hui - Code 4790
M. Piccone - 4040

Defense Advanced Research Projects Agency
1400 Wilson Blvd.
Arlington, Virginia 22209
ATTN: Dr. J. Mangano
Major R. Gullickson

JAYCOR
205 S. Whiting St.
Alexandria, Virginia 22304
ATTN: Drs. D. Tidman
R. Hubbard
S. Slinker

Mission Research Corp.
1720 Randolph Road, S.E.
Albuquerque, NM 87106
ATTN: Dr. Brendan Godfrey
Dr. L. Wright

Pulse Sciences, Inc.
1615 Broadway, Suite 610
Oakland, CA 94612
ATTN: Dr. S. Putnam

McDonnell Douglas Research Laboratories
Dept. 223, Bldg. 33, Level 45
Box 516
St. Louis, MO 63166
ATTN: Dr. Michael Greenspan
Dr. C. Leader

Cornell University
Ithaca, NY 14853
ATTN: Prof. David Hammer

Sandia Laboratories
Albuquerque, NM 87185
ATTN: Dr. Bruce Miller
Dr. Barbara Epstein
Dr. John Olsen
Dr. Don Cook

Beers Associates, Inc.
P. O. Box 2549
Reston, VA 22090
ATTN: Dr. Douglas Strickland

R and D Associates
P.O. Box 9695
Marina del Rey, California 90291
ATTN: Dr. F. Gilmore

Director
Defense Nuclear Agency
Washington, D.C. 20305
ATTN: Dr. C. Fitz (RAAE)
Dr. P. Lunn (RAAE)